

Transport Properties of Droplet Clusters in Gravity-Free Fields

Principal Investigator: Howard Brenner

Abstract

Clusters of liquid droplets are suspended in an atmosphere of saturated vapor and are subjected to an external force field. This system can be modeled as a continuum whose macroscopic properties may be determined by applying the generalized theory of Taylor dispersion.

Background

In many recent studies¹⁻⁴ the phenomenological theory of nucleation⁵ has been derived starting from the more fundamental description of critical phenomena.⁶ In most applications, however, a coarser grained description of the system is required, where the two-phase medium is modeled as a continuum whose macroscopic properties depend on the fine-grained geometric characteristics of the system and on the physical properties of the two phases. In the research program that we have undertaken this goal is pursued for the particular case of liquid droplets immersed in an atmosphere composed of its saturated vapor. This study requires a fundamental understanding of the basic transport processes involved -- specifically, knowledge of the kinetics of phase transformation (involving, for example, rates of droplet coalescence and breakup) and the coupling between such 'internal' transport processes, typically molecular diffusion and convection under the influence of external fields. We expect that the dominance of capillary forces in our two-phase, gravity-free systems will lead to novel physicochemical two-phase interfacial phenomena, not encountered in terrestrial, gravity-dominated systems.

Our approach to the problem uses the following scheme:

- a) Formulate the problem at a microscale level such that the droplets are perceived as discrete entities⁵ and where interfacial effects can be taken into consideration using macroscopic relations.⁷⁻¹³
- b) Apply the generalized theory of Taylor dispersion¹⁴⁻¹⁶ to the problem to obtain a set of model equations (presumably of the convective-diffusive type), describing the system as a continuum at the macroscale.

Results

Our analysis applies to spherical liquid droplets (or vapor bubbles) of radius r at position $R = (s, y, z)$ in a vapor (or liquid) continuum, with σ_0 the surface tension. It begins with the observation that at thermodynamic equilibrium (and in the absence of a gravity field causing sedimentation of the

denser phase) the probability density $P_0^\infty(r)$ for finding droplets of size r at any point R of space is independent of R , and is given by⁵

$$P_0^\infty(r) = C \left\{ \frac{4\pi\sigma_0}{3kT} r^2 \right\}, \quad (1)$$

with kT the Boltzmann factor and C the normalization constant

$$C = 32\pi(\sigma_0/3kT)^{3/2} \quad (2)$$

arising from the unit normalization condition

$$\int_0^\infty P_0^\infty(r) r^2 dr = 1 \quad (3)$$

impose on the probability.

One of our main accomplishments to date is the derivation¹⁷ of the kinetic equation

$$\frac{\delta P}{\delta t} + \nabla \cdot J = \frac{1}{r^2} (r^2 j) = 0 \quad (4)$$

governing the **nonequilibrium** transport of the probability density

$$P = P(r, R, t), \quad (5)$$

$$\int_{R=0}^\infty d^3R \int_{r=0}^\infty P r^2 dr = 1, \quad (6)$$

for finding droplets of size r at position R . In the preceding,

$$\nabla \equiv (\delta/\delta R)_r = i(\delta/\delta x) + j(\delta/\delta y) + k(\delta/\delta z) \quad (7)$$

is the R -space gradient operator, and

$$d^3R = dx dy dz \quad (8)$$

is a physical-space volume element. Here, the convective-diffusive constitutive equation for the fluxes appearing in the conservation equation (4) are, respectively,

(i) size-space flux density:

$$j = uP - d(r) \frac{\delta P}{\delta r}; \quad (9)$$

(ii) physical-space flux density vector:

$$J = U(r)P - D(r)\nabla P. \quad (10)$$

Phenomenological coefficients appearing in the above are with μ_0 the viscosity of the continuous phase,

$$u = - \frac{\sigma_0}{6\mu_0}, \quad (9a)$$

$$d(r) = \frac{kT}{16\pi\mu_0 r} \quad (9b)$$

and

$$U(r) = M(r)F, \quad (10a)$$

$$D(r) = kTM(r), \quad (10b)$$

with

$$M(r) = (6\pi\mu_0 r)^{-1} \quad (10c)$$

the Stokes law mobility of the droplet. In addition, F is the external force, if any, exerted on the droplet.

The zeroth-order moment

$$P_0 \stackrel{\text{def.}}{=} \int_{R=0}^{\infty} d^3R P \quad (11)$$

of the probability density P satisfying the kinetic equation (4)-(10) properly reduces in the steady state, $t \rightarrow \infty$, to the original equilibrium relation (1). On the other hand, if the system is not at equilibrium [e.g. all the droplets are initially of identical size, rather than conforming to the equilibrium size distribution (1)], Eqs. (4)-(10) permit calculation of the detailed relaxation of the droplet size distribution of the system to its equilibrium state (1). Simultaneously, it also allows calculation of the relaxation of spatial gradients existing within the system. In particular, it reveals how these two transport processes are coupled.

Equations (4)-(10) are identical in structure to the generic equations of generalized Taylor dispersion theory,¹⁴⁻¹⁵ thus permitting determination of the macroscopic properties of the two-phase system. For example, we find that the sized-averaged molecular diffusivity,

$$\bar{D}_M \stackrel{\text{def.}}{=} \int_0^{\infty} P_0^{\infty}(r) D(r) r^2 dr, \quad (12)$$

of the system is

$$\bar{D}_M = \frac{2(kT\sigma_0)^{1/2}}{3\sqrt{3}\pi\mu_0}. \quad (13)$$

Moreover, if a force f per unit volume is applied to the discrete phase (i.e. $f = F/(4\pi r^3/3)$), the total diffusivity coefficient \bar{D}^* adopts the form

$$\bar{D}^* = \bar{D}_M + \bar{D}_C, \quad (14)$$

with \bar{D}_C denoting the Taylor-like convective contribution

$$\bar{D}_C = \frac{7}{486\pi^3} \left\{ \frac{3kT}{\sigma_0} \right\}^{5/2} \frac{f^2}{\sigma_0\mu_0} \quad (15)$$

to the diffusion coefficient. It is generally only these mean types of phenomenological quantities that are directly accessible to experiments, rather than comparable size-specific phenomenological coefficients, such as D and d appearing in Eqs. (9) and (10). Closely related to this is the fact that Eqs. (13) and (15) involve only macroscopic physical parameters, namely interfacial tension σ_0 and continuous-phase viscosity μ_0 .

Extensions of the Research

Fundamental solution of the kinetic equation. We are currently attempting to provide the fundamental Green's function solution of the unsteady kinetic equation. by the method of superposition this will reduce the solution of the kinetic equations for an arbitrary initial size

distribution to a quadrature. The existence of such formal solutions will prove useful in future applications by permitting calculation of the relaxation of the system to its equilibrium state.

Finite container size. As in Eq. (3), droplet radii in the range $r = 0$ to ∞ are employed in the development. Obviously, finite container dimensions preclude from consideration relatively large droplet sizes. Thus, in applying our equations in practice, attention needs to be paid to rationally deriving an upper cutoff radius r_0 in relation to the container size.

Lower limit cutoff radius. If the droplets are too small, our kinetic analysis may become inapplicable, owing to the breakdown of the continuum hypothesis. Whether or not such effects are significant remains to be examined.

N particle approach. Hydrodynamic interaction between Brownian droplets. Our ideal kinetic equations effectively represent a one-body particle distribution P . In order to enhance the range of applicability of our analysis we need to create a more general N -body kinetic scheme, in which the (average) number of droplets is not conserved in a nonequilibrium system owing to droplet coalescence and breakup processes. One eventual prediction of our theory should be the **number of droplets** (irrespective of size r) per unit volume at a point R of the continuum, which may prove to be an experimentally accessible quantity. This requires a basic extension of the theory. Among other things, it entails problems of clustering in relation to hydrodynamic interactions among the droplets.

Surfactants. The presence of surface active agents in experimental systems is largely unavoidable. Conversely, the addition of surfactants to two-phase systems often leads to interesting new capillary phenomena, e.g. ultralow tension systems. We intend to investigate the modifications in our theory engendered by the presence of such agents. At a minimum, their presence in the form of an absorbed interfacial phase lowers the surface tension in accordance with Gibb's formula

$$\sigma = \sigma_0 - kT\Gamma_s, \quad (16)$$

where Γ_s is the surface-excess surfactant concentration at the interface. For a fixed mass of surfactant present in the system (assumed to be entirely absorbed at the interface for all times), this has the effect of making δ in Eq. (16) a function of r . As our kinetic theory has involved the assumption that $\sigma \neq \sigma(r)$, necessary modifications of the theory arising from the presence of surfactants will need to be addressed in order to gauge their experimental importance.

Supersaturated systems. Our kinetic approach may provide alternative insights into the standard approaches to the kinetics of phase transitions.¹⁸ Such possibilities will be investigated.

Reference List

1. J.S. Langer, "Kinetics of metastable states," *Systems Far From Equilibrium*, ed. L. Garrido (Berlin:Springer, 1980), pp. 12-47.
2. K. Binder, "Spinodal decomposition," *Systems Far From Equilibrium*, ed L. Garrido (Berlin:Springer, 1989), pp. 76-90.
3. K. Kawasaki and T. Ohta, "Kinetics of fluctuations for systems undergoing phase transitions - Interfacial approach," *Physica* 118A (1983): 175-190.
4. I. Edrei and M. Gitterman, "Transient effects in nucleation for two-dimensional system," *J. Chem. Phys.* 85 (1986): 190-198.
5. *Nucleation*, ed. A.C. Zettlemoyer (New York:Marcel Dekker, 1969).

6. S. Ma, *Modern Theory of Critical Phenomena* (Reading, MA: Benjamin, 1976).
7. H. Brenner, "A micromechanical derivation of the differential equation of interfacial statics," *J. Colloid Interface Sci.* 68 (1979): 422-439.
8. H. Brenner and L.G. Leal, "Interfacial resistance to interphase mass transfer in quiescent two-phase systems," *AIChE J.* 24 (1978): 246-254.
9. H. Brenner and L.G. Leal, "A micromechanical derivation of Fick's law for interfacial diffusion of surfactant molecules," *J. Colloid Interface Sci.* 65 (1978): 191-209.
10. H. Brenner and L.G. Leal, "Conservation and constitutive equations for adsorbed species undergoing surface diffusion and convection at a fluid-fluid interface," *J. Colloid Interface Sci.* 88 (1982): 136-184.
11. S.P. Lin and H. Brenner, "Marangoni convection in a tear film," *J. Colloid Interface Sci.* 85 (1982): 59-65.
12. S.P. Lin and H. Brenner, "Tear film rupture," *J. Colloid Interface Sci.* 89 (1982): 226-231.
13. M. Vignes-Adler and H. Brenner, "A micromechanical derivation of the differential equation of interfacial statics. III. Line tension," *J. Colloid Interface Sci.* 103 (1985): 11-44.
14. H. Brenner, "A general theory theory of Taylor dispersion phenomena," *PhysicoChem. Hydrodyn.* 1 (1980): 91-123.
15. H. Brenner, "A general theory of Taylor dispersion phenomena. II. An extension," *PhysicoChem. Hydrodyn.* 3 (1982): 139-157.
16. H. Brenner, A. Nadim, and S. Haber, "Long-time molecular diffusion, sedimentation and Taylor dispersion of a fluctuating cluster of interacting Brownian particles," *J. Fluid Mech.* (in press, 1986).
17. H. Brenner and R. Mauri, "Size dispersion phenomena in two-phase systems," *J. Colloid Interface Sci.* (in preparation, 1986).
18. J. Heicklen, *Colloid Formation and Growth: A Chemical Kinetics Approach* (New York: Academic, 1976).

List of Publication Support by NSG-7645

1. A. Nadim, "Transport and statistical mechanics of flexible chains and clusters of Brownian particles in quiescent viscous fluids, Ph.D. dissertation, MIT, Cambridge, MA (May 2, 1986), 158pp.
2. H. Brenner, A. Nadim, and S. Haber, "Sedimentation and dispersion of flexible chains and clusters of hydrodynamically-interacting Brownian particles," *Proceedings of the SIAM Conference on Multiphase Systems*, ed. G. Papanicolaou (Philadelphia: SIAM, in press) :21 pp.
3. H. Brenner, A. Nadim, and S. Haber, "Long-time molecular diffusion, sedimentation and Taylor dispersion of a fluctuating cluster of interacting Brownian particles," *J. Fluid Mech.* (submitted, 1986): 93.

4. H. Brenner and R. Mauri, "Size-dispersion phenomena in two-phase systems, *J. Colloid Interface Sci.* (in preparation, 1986).
5. H. Brenner, L. Ting, and D.T. Wasan, "Surface-Excess Interfacial Conservation Laws and Constitutive Equations: A Rational derivation Via Matched Asymptotic Expansions," *Physicochem. Hydrodyn.: Interfacial Phenomena*, Vol. 1, NATO ASI & EPS Conference Proceedings, Huelva, Spain, ed. M. Verlarde (New York:Plenum, in preparation, 1986).